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Orientation of carbazole molecule in the mixed Langmuir-Blodgett films

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Abstract This paper reports the molecular orientation of carbazole (CA) molecules in the mixed Langmuir-Blodgett (LB) films of carbozole in stearic acid (SA) matrix. Changes in the intensities of the absorption bands are observed by rotating the LB films, keeping the direction of the incident radiation unchanged. Maximum intensities of the absorption bands are observed when the LB films are kept at an angle of 45° with the incident radiation. For other angles of orientations , intensities of the absorption bands are minimum. This certainly confirms the fact that CA molecules have preferred orientation on the substrate of the LB films.

Keywords Nonamphiphilic, Langmuir-Blodgett films, UV-Vis absorption spectroscopy

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1. Introduction

Thin films with carefully designed structures and properties have attracted a great deal of interest in recent years due to their potential applications in fabricating various optoelectronic and molecular electronic devices [1-5]. These applications require, in general, well ordered films consisting of molecules with specific properties, carefully aligned with respect to each other and the substrate possessing high degree of stability to thermal and chemical changes. The Langmuir-Blodgett (LB) technique has been used to fabricate the thin films with ideal two dimensional systems, well-controlled composition, structure, thickness and molecular orientations [1]. The bulk properties of the materials incorporated into LB films can be controlled with ease by the organization of molecules in the films and also by changing various LB parameters [1].

Amphiphilic molecules consists of a hydrophilic (water soluble) and a hydro-phobic (water insoluble) parts are the ideal for LB film deposition [1]. However, recent investigations suggest that certain non-amphiphilic molecules when mixed with a long chain fatty acid

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(*e.g.* stearic acid or arachhidic acid) or with an inert polymer matrix (*e.g.* polymethyl methacrylate or polystyrene) form excellent LB films [1,6-7]. These non-amphiphilic molecules are easily available with a wide range of varieties having different interesting physical properties. Also it has been observed that in some cases the optical and electrical characteristics of these non-amphiphilic materials are changed markedly when they are incorporated into some inert matrices or restricted geometry [1,6-7]. Detailed investigations of these non-amphiphilic molecules into restricted geometry of LB films are extremely important from the point of view of their various technical applications. In this paper we report a unique observation of orientation of a well known non-amphiphilic carbazole (CA) molecules in the mixed LB films of CA doped in stearic acid (SA) matrix, using UV-Vis absorption spectroscopy.

Non-amphiphilic CA and its derivative have found extensive technological applications in organic photoconductors [2] and electroluminescent devices [3-5]. They have their unique photophysical characteristics such as intense and well characterized absorption and fluorescence spectra [8-9] Owing to their excellent optical and electronic properties, various derivatives of carbazole were synthesized and studied in the Langmuir-Blodgett films [6, 8-13]. However the orientation of CA molecule in LB films was not studied before.

2. Experimental

CA was purchased from Aldrich Chemical Company, USA and vacuum sublimed followed by repeated recrystalization before use. SA (purity 99%) from sigma, USA, was used as received. The solvent chloroform (SRL, India) was of spectral grade and its fluorescence spectra were checked before use. Langmuir-Blodgett film deposition instrument (Apex, 2000C, India) was used for the study of monolayer characteristics and also for multilayer film deposition. The subphase used was triple distilled deionised water having pH 6.5 in equilibrium with atmospheric carbon dioxide. The solution of CA, SA as well as CA-SA mixtures are prepared in chloroform solvent and were spread on the subphase with the help of micro syringe. Surface pressure was recorded by Wilhelmy plate arrangement described elsewhere [7]. All the films are 10 bilayered. Fluorescence grade quartz slides were used for film deposition and deposition was carried out at a surface pressure of 15 mN/m.

UV-Vis absorption spectra of these films were measured by a Perkin-Elmer Lambda 25 spectrophotometer. All the measurements were performed at room temperature (25°C).

3. Results and discussion

Figure 1 shows the UV-Vis absorption spectra of mixed LB films of CA (0.5 M) in SA matrix placed at angles 0°, 15°, 30°, 45°, 60° and 75° with the incident radiation alongwith the CA solution and microcrystal spectrum for comparison.

Absorption spectrum of CA in chloroform solution shows distinct bands within 225-350 nm region with intense and sharp high energy bands having peaks at 247 and 292 nm alongwith a weak hump at around 258 nm, owing due to S_2-S_1 transition which is directed

parallel to the long axis of the molecule There are two other low intense but prominent vibrational bands in the 300-350 nm regions, with maxima at around 319 nm and 331 nm corresponding to S_1–S_0 transition which is directed parallel to the short axis of the molecule.

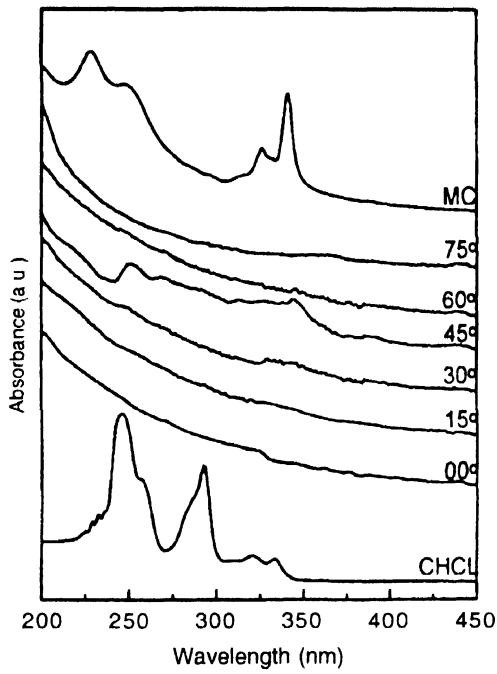

Figure 1 UV-Vis absorption spectra of mixed LB films of CA (0 5 M) in SA matrix placed at angles 0°, 15° 30° 45°, 60° and 75° with the incident radiation alongwith the CA solution and microcrystal spectrum

The CA microcrystal spectrum also shows almost identical vibrational band system except an increase in intensity However, the high energy bands in the microcrystal spectrum become broadened and blue shifted In addition, the band with peak at 292 nm in CA solution spectrum is totally absent in the corresponding microcrystal spectrum This may be due to the aggregation of CA molecules [6]

The absorption spectra of the mixed LB films of CA in SA matrix, kept at various angles with the incident radiation are also shown in Figure 1 Interestingly it was observed that when the mixed LB films were kept at an angle of 45° with the incident radiation prominent vibrational bands are observed both at the high energy and low energy region. These bands are remarkably similar with the microcrystal bands. However, for other angles, namely, 0°, 15°, 30°, 60° and 75° which the films make with the incident radiation, no absorption bands are observed.

The appearance of absorption bands at a particular angle of orientation of the films with the incident radiation definitely concludes the fact that carbazole molecules have a specific orientation in the LB films.

A schematic representation of the alignment of the carbazole (CA) molecules on the substrate of the LB films is shown in Figure 2.

A plausible explanation is that at 45° angle of orientation of the LB films with the incident radiation, the electric field of the incident radiation is along the direction of the dipole moment of the CA molecules. Hence maximum absorption of incident radiation occurred. For other angle of orientation direction of the electric field of the incident radiation does not coincide with the direction of the dipole moment of the CA molecules resulting almost no absorption.

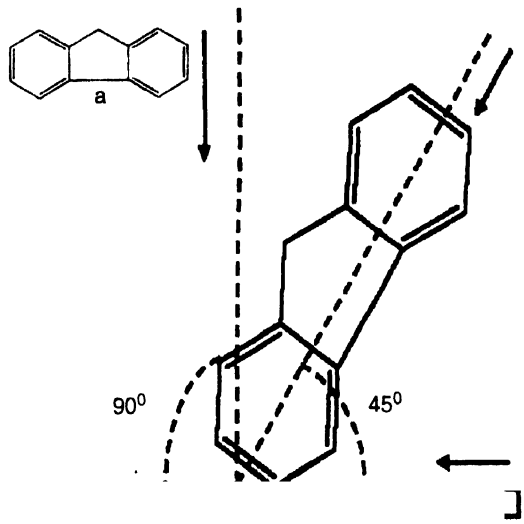

Figure 2. Schematic representation of the alignment of the carbozole (CA) molecule on the substrate of the LB films. Inset shows the molecular structure of CA (a).

4. Conclusion

In conclusion, our results show that carbazole molecules have specific orientation in the mixed LB films. The angle dependence absorption studies of the mixed LB films indicate that when the mixed LB films are kept at an angle of 45° with the incident radiation, prominent absorption bands are observed.

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